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Further Studies of Phase Relations at High Pressure and Temperature in LiAlSiO₄ Eucryptite

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Beamline(s): X17B1

Introduction: The hexagonal aluminosilicate β -eucryptite (LiAlSiO₄) is a structural derivative of β -quartz (SiO₂) such that half of the [SiO₄]⁴⁻ tetrahedra are replaced by [AlO₄]⁵⁻ tetrahedra and the charge is balanced by the incorporation of Li⁺ into the main structural channels parallel to the *c* axis (Buerger, 1954). β -eucryptite has been of continuing interest to mineralogists due to its structural similarity to quartz. Of particular significance to the field of material sciences is its unusual thermal-expansion properties observed at ambient pressure. As already demonstrated by numerous experimental studies, expansion within the (001) plane of the structure is approximately canceled by contraction along the *c* axis, yielding negative thermal expansion along the *c* axis ($\alpha_c \approx -2\alpha_a$) and near-zero volume thermal expansion over a wide temperature range of 300-1400 K.

In a recent study by Zhang et al. (2002), β -eucryptite was found to undergo a reversible polymorphic phase transformation to a previously unknown phase, ϵ -eucryptite. On heating at 13.2 GPa, a complete amorphization was observed in β -eucryptite between 523 and 573 K. On further heating, crystalline phases, spodumene and LiAlO₂ spinel, grew at temperatures between 973-1073 K, which were recovered at ambient conditions. For comparison, Ringwood and Reid (1969) found that eucryptite adopts a spinel structure at 12 GPa and 1273 K. This discrepancy warrants a further study to clarify phase relations of eucryptite at high pressures.

Methods and Materials: The starting β -eucryptite sample was synthesized from Li₂CO₃, Al₂O₃, and SiO₂•nH₂O powders in the molar ratio 1:1:2. The mixture was first sintered at 1373 K for 15 hours and, after regrinding, resintered at 1573 K for 24 hours. X-ray diffraction experiments were performed using a "T-Cup" high-pressure system. An energy-dispersive x-ray method was employed using white radiation at beamline X17B of the National Synchrotron Light Source. NaCl was used as an internal pressure standard, and temperatures were measured by a W/Re25%-W/Re3% thermocouple. In the course of the experiments, the sample was first compressed at room temperature to 18 GPa, followed by heating to the temperature of 1473 K. The procedure was repeated several times at lower pressures.

Results: High-pressure x-ray diffraction patterns revealed that β -eucryptite underwent progressive amorphization at pressures above 3 GPa on room temperature compression and became complete amorphous at pressures higher than 18 GPa. On heating at 18 GPa, the sample remained to be an amorphous phase up to 1073 K. Upon further heating, crystal growth was observed and all diffraction lines can be indexed with a single phase of spinel structure. The spinel phase of LiAlSiO₄ was found to be stable in the pressure range of 14-16 GPa up to 1473 K. At lower pressures and 1273 K, the spinel phase decomposed into a mixture of spodumene and LiAlO₂ spinel. The pressure-volume-temperature data were collected for LiAlSiO₄ spinel up to 1473 K at 14-17 GPa.

Conclusions: The present study confirms previous finding of Ringwood and Reid (1969), in that the two phase mixture of spodumene and LiAlO₂ spinel would recombine into a single phase of spinel structure. By analog with findings in NaAlSiO₄ (Akaogi et al., 2001) and MgAl₂O₄ (Irifune et al, 2002), one may expect that at further higher pressures LiAlSiO₄ spinel may either transform to a calcium-ferrite phase or decompose into a mixture of its constituent oxides.

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References: Akaogi et al., Phys. Earth Planet. Int. 130, 49-58, 2001. Buerger, M.J., Am. Mineral., 39, 600-614, 1954. Irifune et al., Phys. Chem. Minerals, in press. Ringwood and Reid, Earth Planet. Sci. Lett. 5, 245-250 (1969). Zhang et al., Am. Mineral. 87, 566-571 (2002).